



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-670711

Anonymous Referee Report

J. G. Tobin

May 14, 2015

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Ms. Ref. No.: ELSPEC-D-15-00086

Journal of Electron Spectroscopy and Related Phenomena

Title: Electronic structure and chemical bond nature in $\text{Cs}_2\text{PuO}_2\text{Cl}_4$

Authors: Yu.A. Teterin, A.Yu. Teterin, K.E. Ivanov, M.V. Ryzhkov, K.I. Maslakov, St.N. Kalmykov, V.G. Petrov, D. N. Suglov

Institutions: NRC "Kurchatov Institute", Moscow, 123182, Russia, Ural Department of RAS, Institute of Solid State Chemistry, Ekaterinburg, 620990 Russia, Chemistry Department, Lomonosov Moscow State University, Moscow, 119991 Russia, V.G. Khlopin Radium Institute, St.-Petersburg, Russia

This is a combined experimental and theoretical study of the compound $\text{Cs}_2\text{PuO}_2\text{Cl}_4$, using X-ray Photoelectron Spectroscopy (XPS) and Relativistic Discrete Variation (RDV) calculations. Here, the Pu has an oxidation state of six (Pu(VI)) with a formal charge of Pu^{+6} . The compound includes a plutonyl structure (PuO_2^{-2}). The RDV calculational method utilizes a cluster approach with "natural" orbitals, retaining their nature of orbital and spin angular momenta. The RDV method produces results showing the overlap of atomic orbitals over an energy range of several 10's of eV, giving rise to outer valence molecular orbitals (OVMO), nearer the Fermi Energy, and inner valence molecular orbitals (IVMO), with shallow core levels involved. It should be noted that Pu is a difficult material with which to work, being chemically toxic, radiologically active and pyrolytic (prone to catch fire). This is an excellent piece of work and should be published in JESRP. However, there are some significant issues that need to be addressed and mandatory changes are required. Here are some specifics, not necessarily in the order of importance.

1. The English needs to be improved. The referee is completely incapable of writing a manuscript in Russian, so this demand is inherently unfair. However, to optimize the dispersal of this technical information, a version with enhanced English is required.
2. The authors overuse the word "structure." It appears that they often mean "spectral structure," but occasionally it takes on other roles as

- well. The problem is that in English scientific parlance, “structure” usually means a geometrical or physical arrangement, such as the arrangement of atoms found from an EXAFS analysis.
3. Please make future manuscripts at least 1.5 spaced, not single-spaced.
 4. Page 2, Paragraph 1, line 16: Computational methods each have approximations in their arithmetic, limitations in what the results mean and inherent biases. The RDV method has the great advantage of having “natural wavefunctions.” However, the referee has trouble accepting the notion that the U6p’s, with a binding energy of 20 eV, are involved with the chemical bond. This looks like one of those calculational biases that crop up occasionally.
 5. Page 3, Paragraph 1, line 4: “solved” -- > “dissolved.”
 6. Page 3, Paragraph 2: Is the spectrometer one of those HP systems with the crystal wavelength selector on the photon input and dispersion compensation on the electron energy analyzer side? If so, this should be noted. This information would support the claim of an energy resolution of 0.7eV.
 7. Page 3, Paragraph 2, line 6: intense should be intensity.
 8. Page 3, Paragraph 2, line 8: giver should be given.
 9. Page 4, Paragraph 4: What do you mean by many-body? Is this harking back to the work by people such as Ward Plummer showing many-body behavior in the valence states of alkalis and aluminum?
 10. Page 5, Paragraph 1, line 1: “can determine the actinide ion oxidation state.” Please describe how.
 11. Page 7, paragraph 1: What are these “dynamic effects?”
 12. On pages 5 and 7: There are no figures for the 5p and 5s spectra, only numbers in the tables. Maybe the spectra should be shown.
 13. Regarding spectra: perhaps the spectra for the compound should be plotted along with the spectra from the other materials that are discussed in the text, e.g. Pu metal, PuO₂ etc.
 14. Page 8, Paragraph 2: The electronic configuration is founded upon a

Russell Saunders picture, where $\frac{1}{2}$ filling is associated with $n(5f) = 7$. However, much new data suggests that the correct picture for the 5f's is an intermediate case with a tendency towards jj-coupling. (For example, see van der Laan et al, PRL 2004.) Maybe the underlying assumption in the electronic configuration and the contrary data should be mentioned.

15. Page 8, paragraph 2, line 14: americium? In a Pu compound cluster?
16. Page 11, Paragraph 4: "can be explained by the fact that the Pu 5f electrons do not lose their f-nature participating in the chemical bond." Didn't Barry Cooper publish calculations many years ago about 5f-6d hybridization in chemical bonds? It would be good to discuss this.
17. Page 13, Paragraph 3, line 11: "These results yield a conclusion that the Pu 5f electrons can participate directly in the chemical bond formation in PuO_2Cl_4 partially losing the f-nature." Same as 16 above.
18. Page 15, paragraph 1, line 17: "However, these data show that the $21\gamma_6(4)$ IVMO has a significant antibonding nature." This goes back to #4 above: Is there enough anti-bonding nature to get a cancellation in the IVMO so that it reverts back to atomic orbital behavior?
19. Page 16, paragraph 2, line 7: "Despite the fact that the share of the 5f AO is greater than that of the 6d AO, their contributions are comparable and the last $23\gamma_6$ -orbital shows the least orbital force (0.22° — 10^{-8} N) among the six considered bonding MOs." Please explain.
20. Page 16, end of paragraph 2: "Despite the approximation used for the evaluation of these data was not perfect, one can conclude that the theoretical and experimental studies of chemical bond cannot neglect the IVMO formation effect in actinide compounds." The referee may not be convinced, but the authors have the right to say so.
21. Page 17: acknowledgement is misspelled. (Missing an "n.")